

# Electronic states of metallic and semiconducting carbon nanotubes with bond and site disorder

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## Abstract

Disorder effects on the density of states in carbon nanotubes are analyzed by a tight binding model with Gaussian bond or site disorder. Metallic armchair and semiconducting zigzag nanotubes are investigated. In the strong disorder limit, the conduction and valence band states merge, and a finite density of states appears at the Fermi energy in both of metallic and semiconducting carbon nanotubes. The bond disorder gives rise to a huge density of states at the Fermi energy differently from that of the site disorder case. Consequences for experiments are discussed.

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# I. Introduction

Recently, carbon nanotubes with cylindrical graphite structures have been intensively investigated. Many interesting experimental as well as theoretical researches have been performed (see reviews [1,2] for example), and the fundamental metallic and semiconducting behaviors of single wall nanotubes predicted by theories [3-8] have been clarified in tunneling spectroscopy experiments [9,10].

In the preceding work [11], we have studied changes of the density of states and electronic conduction in metallic carbon nanotubes with using a tight binding model with Gaussian bond disorder. Metallic armchair and zigzag nanotubes have been investigated. We have obtained a conductance which becomes smaller by the factor  $1/2 - 1/3$  from that of the clean nanotube. We have also found that suppression of electronic conductance around the Fermi energy due to disorder is smaller than that of the inner valence (and conduction) band states, as a consequence of the extended nature of electronic states around the Fermi energy between the valence and conduction bands, and is a property typical of the electronic structures of metallic carbon nanotubes.

The purpose of this paper is to give calculations on semiconducting carbon nanotubes newly, which have not been studied in the previous report [11]. Site as well as bond disorder effects on the density of states of metallic and semiconducting nanotubes are considered. The bond and site disorder model has been used in the discussion of polarons in doped  $C_{60}$  [12], too. We will discuss the following. In the strong disorder limit, the conduction and valence band states merge, and a finite density of states appears at the Fermi energy in both of metallic and semiconducting carbon nanotubes. A huge density of states appears at the Fermi energy in the bond disorder case. This property does not occur for the site disorder case. Consequences for experiments are discussed.

## II. Model

We will study the following model for carbon nanotubes with bond disorder:

$$H = -t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.}) + \sum_{\langle i,j \rangle, \sigma} \delta t_{i,j} (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.}). \quad (1)$$

The first term is the tight binding model with the nearest neighbor hopping interaction  $t$ ; the sum is taken over neighboring pairs of lattice sites  $\langle i, j \rangle$  and spin  $\sigma$ ;  $c_{j,\sigma}$  is an annihilation operator of an electron with spin  $\sigma$  at the site  $i$ . The second term is the bond disorder model, and the hopping interaction  $\delta t_{i,j}$  obeys the Gaussian distribution function

$$P(\delta t) = \frac{1}{\sqrt{4\pi}t_s} \exp\left[-\frac{1}{2}\left(\frac{\delta t}{t_s}\right)^2\right] \quad (2)$$

with the strength  $t_s$ .

In the site disorder case, the model hamiltonian is:

$$H = -t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{h.c.}) + \sum_{i,\sigma} \delta U_i c_{i,\sigma}^\dagger c_{i,\sigma}, \quad (3)$$

where  $\delta U_i$  is the onsite potential due to site disorder whose distribution is the Gaussian function with the strength  $U_s$ .

A finite system with the quite large system size  $N$  of metallic carbon nanotubes is diagonalized numerically. In this paper, we take  $N = 4000$  for the (5,5) metallic nanotube, and for the (10,0) semiconducting zigzag tube. The quantity  $t_s$  is changed within  $0 \leq t_s \leq 1t$ , and  $U_s$  is varied within  $0 \leq U_s \leq 1t$ . All the quantities with the dimension of energy are measured in units of the hopping integral  $t$  ( $\sim 2$  eV) in this paper.

## III. Bond disorder effects

Figure 1 shows the density of states (DOS) of the metallic (5,5) nanotube with bond disorder. Figures 1 (a), (b), and (c) show the weak disorder case with  $t_s = 0.1t$ , the middle strength case  $t_s = 0.5t$ , and the strong limit case  $t_s = 1.0t$ , respectively. When  $t_s = 0.1t$ , the DOS retains its one-dimensional singularities. The magnitude of the constant DOS around the Fermi energy

$E = 0$  is near to that of the clean system. As  $t_s$  increases, the DOS of the valence and conduction band states broadens. In the case of  $t_s = 0.5t$  (Fig. 1 (b)), the DOS is very broad and loses the one-dimensional characters. The magnitude of the DOS at the Fermi energy does not decrease, but it enhances from that of the clean system. This is due to the large overlap of the original valence and conduction band states. In the strong  $t_s$  case (Fig. 1 (c)), we find a *surprising sharp peak* at the Fermi energy. This is not an accidental result of the calculation. The peak value of the DOS is a few times larger than that of the bodies of the valence and conduction band states at  $t_s = 1.0t$ . The DOS at the Fermi energy is more than ten times larger at  $t_s = 1.0t$  than that of the clean system  $t_s = 0$ .

Next, we consider the DOS of the semiconducting (10,0) nanotube with bond disorder. Fig. 2 shows the calculated DOS for the three disorder strengths. In the weak disorder case  $t_s = 0.1t$  (Fig. 2 (a)), the DOS well retains its one-dimensional features. However, as the disorder strength becomes larger, the energy gap decreases. And, a finite density of states is present at the center of energy as shown for the case  $t_s = 0.5t$  (Fig. 2 (b)). This merging of the valence and conduction band states might mean a kind of insulator-semimetal transitions. Here, the transition to a semimetal simply refers to an appearance of a finite density of states around the Fermi energy in the presence of disorder potentials. In the strong disorder case (Fig. 2 (c)), we again find a *huge density of states* at the origin of energy. Such the common result between the metallic and semiconducting nanotubes might mean that the feature at the strong disorder limit does not depend on whether the clean system is metallic or not.

It is interesting to look at the disorder strength dependence of the DOS, and compare the two cases of the metallic and semiconducting carbon nanotubes (Figs. 1 and 2). Figure 3 show the variations as a function of the bond disorder strength  $t_s$ . Squares are for the metallic (5,5) nanotube, and crosses are for the semiconducting (10,0) nanotube. In the weak disorder region ( $t_s < 0.4t$ ) of the (5,5) nanotube, the density of states is nearly constant due to the flatness around the Fermi energy (Fig. 1 (a)). After merging the valence and conduction band states ( $t_s > 0.5t$ ), the DOS becomes more than one order of magnitudes larger owing to the

appearance of the huge peak (Fig. 1 (c)). The DOS even becomes about ten times larger than that of the clean metallic system. For the semiconducting (10,0) nanotube, the DOS at the gap center is negligible when  $t_s < 0.4t$ . The development of the density of states after the insulator-semimetal transition is very similar to that of the metallic (5,5) system. The similarity is quantitatively as well as qualitatively. Such the similarity indicates that the result in the strong  $t_s$  limit is general as the bond disorder effects, not depending on whether the clean system is metallic or not.

## IV. Site disorder effects

In this section, we turn to the site disorder effects. As in the previous section, results of the (5,5) metallic nanotube are reported in Fig. 4, and those of the (10,0) semiconducting nanotube are reported in Fig. 5. The disorder strengths are  $U_s = 0.1t$  (Figs. 4 (a) and 5 (a)),  $U_s = 0.5t$  (Figs. 4 (b) and 5 (b)), and  $U_s = 1.0t$  (Figs. 4 (c) and 5 (c)), respectively. In the weak disorder case ( $U_s = 0.1t$ ), one-dimensional features in the entire density of states can be seen clearly. As the strength becomes larger, the merging of the valence and conduction bands occurs (Figs. 4 (b) and 5 (b)). A kind of insulator-semimetal transition is found for Fig. 5, as in the bond disorder case. Then, the entire DOS becomes very broad in the strong disorder limit (Figs. 4 (c) and 5 (c)). We thus find a *qualitative difference* from that of the bond disorder case: the absence of the huge peak around the energy center. Rather, the site impurity effects on the DOS seem usual as general theories of disorder predict.

Finally, Figure 6 shows the disorder strength  $U_s$  dependence of the DOS at the Fermi energy. Squares are for the (5,5) nanotube, and the crosses are for the (10,0) nanotube. The nearly constant behavior in the weak disorder region of the (5,5) nanotube case is similar to that of the bond disorder effect. In the strong disorder ( $U_s \sim 1.0t$ ), the DOS enhances its magnitude more or less from that of the weak disorder. However, the order of the magnitudes is the same. In the (10,0) tube case, the transition to the semimetal occurs at  $U_s = 0.6t$ . The DOS of the

strong  $U_s$  region is like that of the squares. The magnitude of the DOS is of the same order, even if we do calculations for the disorder strengths upto  $U_s \sim 5t$ . Therefore, we conclude that a huge density of states does not appear in the site disorder case differently from the bond disorder effects.

The bond and site disorder effects in the weak strength region are similar mutually as we expect from general theory of disorder systems. However, there is a remarkable difference in the strong disorder limit. This might come from the difference of how the disorder potential works. In the literature [13], a one dimensional system with bond disorder has been analyzed. The analytic formula shows the logarithmic divergence of the DOS at the Fermi energy. The similar effect might take place in the present numerical calculations of carbon nanotubes with bond disorder.

In the real carbon nanotubes, bond as well as site disorder can be present simultaneously, even though the two strengths might be different. In cases with stronger bond disorder and weak site disorder, we might be able to find a large density of states at the energy center. Here, an originally semiconducting system could exhibit a finite density of states. Such an observation seems interesting if some kinds of measurements are possible.

## V. Summary

In summary, we have investigated disorder effects on the density of states in metallic and semiconducting carbon nanotubes, using a tight binding model with Gaussian bond or site disorder. Armchair and zigzag nanotubes have been considered. The systems with weak disorder are similar in both disorder cases. However, as the disorder becomes stronger the conduction and valence band states merge, and a finite density of states appears at the Fermi energy in both of metallic and semiconducting carbon nanotubes. The bond disorder gives rise to a huge density of states at the Fermi energy differently from that of the site disorder case.

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## Figure Captions

Fig. 1. Density of states (DOS) of the (5,5) nanotube with bond disorder. Figs. (a), (b), and (c) show the cases with  $t_s = 0.1t$ ,  $0.5t$ , and  $1.0t$ , respectively.

Fig. 2. Density of states (DOS) of the (10,0) nanotube with bond disorder. Figs. (a), (b), and (c) show the cases with  $t_s = 0.1t$ ,  $0.5t$ , and  $1.0t$ , respectively.

Fig. 3. Density of states (DOS) at the Fermi energy  $E = 0$  as a function of  $t_s$ . Squares and crosses show the results of the (5,5) and (10,0) nanotubes, respectively.

Fig. 4. Density of states (DOS) of the (5,5) nanotube with site disorder. Figs. (a), (b), and (c) show the cases with  $U_s = 0.1t$ ,  $0.5t$ , and  $1.0t$ , respectively.

Fig. 5. Density of states (DOS) of the (10,0) nanotube with site disorder. Figs. (a), (b), and (c) show the cases with  $U_s = 0.1t$ ,  $0.5t$ , and  $1.0t$ , respectively.

Fig. 6. Density of states (DOS) at the Fermi energy  $E = 0$  as a function of  $U_s$ . Squares and crosses show the results of the (5,5) and (10,0) nanotubes, respectively.